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Role of partial miscibility on pressure buildup due to constant rate injection of CO₂ into closed and open brine aquifers

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[1] This work extends an existing analytical solution for pressure buildup because of CO₂ injection in brine aquifers by incorporating effects associated with partial miscibility. These include evaporation of water into the CO₂ rich phase and dissolution of CO₂ into brine and salt precipitation. The resulting equations are closed-form, including the locations of the associated leading and trailing shock fronts. Derivation of the analytical solution involves making a number of simplifying assumptions including: vertical pressure equilibrium, negligible capillary pressure, and constant fluid properties. The analytical solution is compared to results from TOUGH2 and found to accurately approximate the extent of the dry-out zone around the well, the resulting permeability enhancement due to residual brine evaporation, the volumetric saturation of precipitated salt, and the vertically averaged pressure distribution in both space and time for the four scenarios studied. While brine evaporation is found to have a considerable effect on pressure, the effect of CO₂ dissolution is found to be small. The resulting equations remain simple to evaluate in spreadsheet software and represent a significant improvement on current methods for estimating pressure-limited CO₂ storage capacity.

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1. Introduction

[2] A critical design aspect of CO₂ storage systems is that pressure buildup because of CO₂ injection should not exceed the fracture pressure of the overlying caprock [Mathias *et al.*, 2009a, 2009b]. The conventional approach to assessing pressure buildup involves applying a numerical reservoir simulator [Rutqvist *et al.*, 2007, 2008]. Another approach is to numerically integrate the closed-form pressure gradient expression resulting from the Buckley and Leverett [1942] (BL) equation [Saripalli and McGrail, 2002]. Simplifying assumptions associated with the BL equation include: vertical pressure equilibrium, negligible capillary pressure, incompressible flow, and immiscible displacement. Following an energy minimization approach, Nordbotten *et al.* [2005] derived a similar integral expression, representing a special case of the BL equation where relative permeability is assumed to be a linear function of fluid saturation.

[3] Mathias *et al.* [2009c] applied the method of matched asymptotic expansions to extend Nordbotten's method, to account for moderate fluid and rock compressibility, giving rise to a closed-form pressure buildup equation for CO₂

injection into brine aquifers of infinite lateral extent. Compressibility was assumed large enough that the aquifer has the capacity to retard pressure waves but small enough that fluid density and rock porosity can be assumed constant, the situation generally assumed for most groundwater problems.

[4] More recently, following Ehlig-Economides and Economides [2010], Mathias *et al.* [2011] improved their analysis further by invoking a quasi-steady state assumption, allowing the development of a closed-form solution, which takes into account the presence of a far-field impermeable boundary. To properly explore the implications of their simplifying model assumptions, Mathias *et al.* [2011] compared their results with those from the numerical simulator TOUGH2 [Pruess *et al.*, 1999] using the equation of state module, ECO2N [Pruess, 2005; Pruess and Spycher, 2007]. The assumptions of vertical pressure equilibrium and negligible capillary pressure were found to not significantly affect the pressure buildup estimation. The assumption of constant fluid properties worked well providing an estimate of final pressure that was used to calculate CO₂ fluid properties. The assumption of immiscible flow was also found to be appropriate, providing enough time had passed for the pressure perturbation to reach the outer impermeable boundary of the reservoir. But prior to that, ignoring partial miscibility led to an overestimation of pressure. Permeability reduction due to salt precipitation was ignored.

[5] Miscibility of CO₂ with water leads to CO₂ partially dissolving in brine and water partially vaporizing in the presence of CO₂ [Spycher *et al.*, 2003; Spycher and Pruess,

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2005]. Because of the large interfacial area between the brine and CO₂ that develops at the porescale, it is often assumed that the two phases are in equilibrium with one another. Such a hypothesis gives rise to the CO₂ injection leading to a three-region system [see Figure 2 of *Noh et al.*, 2007]. (1) A dry-out zone develops around the well where all water has been either displaced or vaporized. (2) Surrounding this is a region that contains both a CO₂ rich phase (hereafter referred to as the gas phase) and an aqueous phase. The gas phase contains mostly CO₂ but also contains water at the water in CO₂ solubility limit. The aqueous phase contains mostly brine but also contains CO₂ at the CO₂ in brine solubility limit. (3) Surrounding the two-phase region is another region that contains only brine and is completely free from CO₂.

[6] Although the dry-out zone is free of water, the salt that previously resided in brine remains precipitated in the porespace. Salt precipitation leads to a loss of permeability [Pruess and Muller, 2009; Pruess, 2009; Zeidouni et al., 2009] and hence a loss in injectivity. But in the numerical study of *Mathias et al.* [2011], accounting for partial miscibility led to an increase in injectivity. This was partially because of the reduction in volumetric flow rate that results from dissolution of CO₂ in brine, but mostly because the dry-out zone had consumed residually trapped brine around the injection well. Residual brine saturations, following CO₂ injection in Canadian sandstones, have been observed as high as 66%, resulting in losses in permeability as high as 90% [Bennion and Bachu, 2008]. It can therefore be understood that removal of residual brine by evaporation can potentially lead to significant increases in relative permeability.

[7] *Noh et al.* [2007] and *Pruess* [2009] derived analytical solutions using fractional flow theory [Orr, 2007] to look at the effects of partial miscibility on gas saturation distribution assuming no volume change occurs on fluid mixing. *Zeidouni et al.* [2009] improved on these by rigorously satisfying mass continuity and properly accounting for volume change on fluid mixing using methods specified by *Orr* [2007].

[8] Clearly, it would be advantageous to extend the pressure build-up equations of *Mathias et al.* [2009c, 2011] to account for partial miscibility of CO₂ with brine. The pressure buildup equations of *Burton et al.* [2008] and *Ehlig-Economides and Economides* [2010] account for partial miscibility in this way. However, their solutions rely on the specification of a heuristic function to describe relative permeability distribution in space. Furthermore, volume change on fluid mixing is ignored and the location of leading and trailing shock fronts (explained in more detail in section 3) must be specified by a graphical method or an iterative procedure. In this article, the pressure buildup equations of *Mathias et al.* [2009c, 2011] are extended to account for CO₂ brine partial miscibility without the use of heuristic functions. Furthermore, mass balance is rigorously satisfied and closed-form solutions are derived for the locations of the associated shock fronts.

[9] The structure of this article is as follows. The relevant governing equations for two-component two-phase fractional flow are presented. The locations of trailing and leading shock fronts, along with associated changes in volumetric flux, are found by consideration of global mass balance expressions. Linear relatively permeability functions

are described and placed in the context of more general power law relative permeability functions. Closed-form solutions for the locations of the shock fronts are obtained. The model is linked with a compressible brine aquifer model and integrated to obtain a closed-form solution for pressure. A comparison of results is made with those obtained using TOUGH2 ECO2N.

2. Two-Component Two-Phase Flow

[10] In section 2, we closely follow the work of *Zeidouni et al.* [2009]. The mass continuity equations for CO₂ and water for one-dimensional, radially symmetric, incompressible, two-phase, two-component radial flow can be written as (adapted from chapter 2 of *Orr*, [2007]),

$$\phi \frac{\partial}{\partial t} (\omega_{ca} \rho_a S_a + \omega_{cg} \rho_g S_g) = -\frac{1}{r} \frac{\partial}{\partial r} [r (\omega_{ca} \rho_a q_a + \omega_{cg} \rho_g q_g)], \quad (1)$$

$$\phi \frac{\partial}{\partial t} (\omega_{wa} \rho_a S_a + \omega_{wg} \rho_g S_g) = -\frac{1}{r} \frac{\partial}{\partial r} [r (\omega_{wa} \rho_a q_a + \omega_{wg} \rho_g q_g)], \quad (2)$$

where ϕ [–] is porosity, t [T] is time, r [L] is radial distance, ω_{ca} [–], ω_{wa} [–], ω_{cg} [–], ω_{wg} [–], are the mass fractions of CO₂ (subscript c) and water (subscript w) in the aqueous (subscript a) and gas (CO₂ rich) (subscript g) phase, respectively, and S_a [–], q_a [LT^{–1}], S_g [–], q_g [LT^{–1}] are the volumetric saturations and fluxes of the aqueous and gas phase, respectively.

[11] Note that here we have assumed radial symmetry. For very large viscosity differences, viscous fingering will occur and the problem will not be radially symmetric as planned [Zhang et al., 1997].

[12] The mass fractions and volumetric saturations are interrelated by $\omega_{ca} + \omega_{wa} + \omega_{sa} = 1$, $\omega_{cg} + \omega_{wg} = 1$, and $S_a + S_g + S_s = 1$ where ω_{sa} [–] is the mass fraction of salt in the aqueous phase and S_s [–] is the volumetric saturation of precipitated salt. Note that although the fluids are assumed incompressible, it is necessary to keep fluid density within the derivatives due to density changes associated with changes in composition.

[13] Introducing the similarity transform

$$z = \frac{\pi \phi \rho_c H r^2}{M_0 t}, \quad (3)$$

allows the above equations to reduce to [Orr, 2007, chapter 4]

$$z = \frac{dH_c}{dG_c} = \frac{dH_w}{dG_w}, \quad (4)$$

where M_0 [MT^{–1}] is a constant mass injection rate of CO₂ of density, ρ_c , [ML^{–3}], H [L] is the thickness of the formation being injected into, and the G and H functions are defined by

$$G_c = c_{ca} S_a + c_{cg} S_g, \quad H_c = q_D a_c, \quad (5)$$

$$G_w = c_{wa} S_a + c_{wg} S_g, \quad H_w = q_D a_w, \quad (6)$$

where

$$a_c = c_{ca}f_a + c_{cg}f_g, \quad a_w = c_{wa}f_a + c_{wg}f_g, \quad (7)$$

and f_a and f_g are the fractional flows of aqueous and gas phase, found from

$$f_a = \frac{q_a}{q_a + q_g}, \quad f_g = \frac{q_g}{q_a + q_g}, \quad (8)$$

and

$$c_{ca} = \frac{\omega_{ca}\rho_a}{\rho_c}, \quad c_{wa} = \frac{\omega_{wa}\rho_a}{\rho_c}, \quad (9)$$

$$c_{cg} = \frac{\omega_{cg}\rho_g}{\rho_c}, \quad c_{wg} = \frac{\omega_{wg}\rho_g}{\rho_c}, \quad (10)$$

$$q_D = \frac{2\pi\rho_c H r(q_a + q_g)}{M_0}. \quad (11)$$

3. Location of Shocks and Evaluation of q_D

[14] The two-phase two-component system under consideration gives rise to both trailing and leading shocks [Noh *et al.*, 2007; Zeidouni *et al.*, 2009; Orr, 2007]. The locations of the leading and trailing shocks, denoted z_L and z_T are the locations (in similarity space), respectively, and can be found from the mass balance equations (similar to Brinkman [1949]):

$$H_{c1} - H_{c3} = G_{c1}z_T + \int_{z_T}^{z_L} G_c dz - G_{c3}z_L, \quad (12)$$

$$H_{w1} - H_{w3} = G_{w1}z_T + \int_{z_T}^{z_L} G_w dz - G_{w3}z_L, \quad (13)$$

where $G_{c1} = G_c(z = 0)$, $G_{w1} = G_w(z = 0)$, $H_{c1} = H_c(z = 0)$, and $H_{w1} = H_w(z = 0)$, describe the physical state of the injection fluid and $G_{c3} = G_c(z \rightarrow \infty)$, $G_{w3} = G_w(z \rightarrow \infty)$, $H_{c3} = H_c(z \rightarrow \infty)$, and $H_{w3} = H_w(z \rightarrow \infty)$ describe the physical state of the initial reservoir fluid.

[15] Applying the chain rule we have

$$\int_{z_T}^{z_L} G_c dz = \int_{G_{cT}}^{G_{cL}} G_c \frac{dz}{dG_c} dG_c, \quad (14)$$

where $G_{cT} = G_c(z = z_T)$ and $G_{cL} = G_c(z = z_L)$.

[16] The application of integration by parts then leads to

$$\int_{G_{cT}}^{G_{cL}} G_c \frac{dz}{dG_c} dG_c = [G_c z]_{G_{cT}}^{G_{cL}} - \int_{G_{cT}}^{G_{cL}} z dG_c, \quad (15)$$

and substituting equation (4) yields (similar to Welge [1952])

$$[G_c z]_{G_{cT}}^{G_{cL}} - \int_{G_{cT}}^{G_{cL}} z dG_c = [G_c z - H_c]_{G_{cT}}^{G_{cL}}, \quad (16)$$

therefore,

$$\int_{z_T}^{z_L} G_c dz = G_{cL}z_L - H_{cL} - G_{cT}z_T + H_{cT}, \quad (17)$$

where $H_{cT} = H_c(z = z_T)$ and $H_{cL} = H_c(z = z_L)$.

[17] Substituting equation (17) into equation (12), yields

$$H_{c1} - H_{c3} = G_{c1}z_T + G_{cL}z_L - H_{cL} - G_{cT}z_T + H_{cT} - G_{c3}z_L. \quad (18)$$

[18] Similarly, from equation (13), we have

$$H_{w1} - H_{w3} = G_{w1}z_T + G_{wL}z_L - H_{wL} - G_{wT}z_T + H_{wT} - G_{w3}z_L, \quad (19)$$

where $G_{wT} = G_w(z = z_T)$, $G_{wL} = G_w(z = z_L)$, $H_{wT} = H_w(z = z_T)$, and $H_{wL} = H_w(z = z_L)$.

[19] To derive an expression for the location of the trailing front, z_T , consider the mass conservation statements for CO_2 and water in the region $0 \leq z \leq z_T$:

$$H_{c1} - H_{cT} = (G_{c1} - G_{cT})z_T, \quad (20)$$

$$H_{w1} - H_{wT} = (G_{w1} - G_{wT})z_T. \quad (21)$$

[20] Rearranging leads to

$$z_T = \frac{H_{c1} - H_{cT}}{G_{c1} - G_{cT}} = \frac{H_{wT} - H_{w1}}{G_{wT} - G_{w1}}, \quad (22)$$

which on substitution back into equations (18) and (19) gives

$$z_L = \frac{H_{cL} - H_{c3}}{G_{cL} - G_{c3}} = \frac{H_{w3} - H_{wL}}{G_{w3} - G_{wL}}. \quad (23)$$

[21] Under such conditions, q_D is piecewise and can be defined by

$$q_D = \begin{cases} q_{D1}, & 0 \leq z < z_T \\ q_{D2}, & z_T \leq z \leq z_L \\ q_{D3}, & z > z_L \end{cases} \quad (24)$$

and from equations (23) and (22) it can be shown that

$$\frac{q_{D2}a_{cL} - q_{D3}a_{c3}}{G_{cL} - G_{c3}} = \frac{q_{D3}a_{w3} - q_{D2}a_{wL}}{G_{w3} - G_{wL}}, \quad (25)$$

$$\frac{q_{D1}a_{c1} - q_{D2}a_{cT}}{G_{c1} - G_{cT}} = \frac{q_{D2}a_{wT} - q_{D1}a_{w1}}{G_{wT} - G_{w1}}, \quad (26)$$

which, on solving for q_{D2} and q_{D3} lead to [Orr, 2007; Zeidouni *et al.*, 2009]

$$q_{D3} = q_{D2} \left[\frac{a_{wL}(G_{cL} - G_{c3}) + a_{cL}(G_{w3} - G_{wL})}{a_{w3}(G_{cL} - G_{c3}) + a_{c3}(G_{w3} - G_{wL})} \right], \quad (27)$$

$$q_{D2} = q_{D1} \left[\frac{a_{w1}(G_{c1} - G_{cT}) + a_{c1}(G_{wT} - G_{w1})}{a_{wT}(G_{c1} - G_{cT}) + a_{cT}(G_{wT} - G_{w1})} \right]. \quad (28)$$

Note that in the dryout-zone ($z < z_T$), volumetric flow rate is unchanged from at the injection point, therefore, $q_{D1} = 1$.

[22] The region where f_g is a differentiable function of S_g is often referred to as the spreading wave [Orr, 2007]. Within the spreading wave, from equation (4), it can be shown that [Orr, 2007]

$$z = \frac{dH_c}{dG_c} = q_D \frac{df_g}{dS_g}, \quad (29)$$

from which it follows that, providing the shocks are either followed or led by a spreading wave

$$z_L = q_{D2} \frac{df_g}{dS_g} \Big|_{S_g=S_{gL}} \quad \text{and} \quad z_T = q_{D2} \frac{df_g}{dS_g} \Big|_{S_g=S_{gT}}. \quad (30)$$

[23] Substituting these into equations (23) and (22), and considering the definitions provided in equations (5) and (6), gives rise to

$$\frac{df_g}{dS_g} \Big|_{S_g=S_{gs}} = \frac{A_1 + A_2 f_g(S_g=S_{gs})}{A_3 + A_2 S_{gs}}, \quad (31)$$

where

$$\begin{aligned} A_1 &= c_{ca} - (q_{D3}/q_{D2})a_{c3}, & A_2 &= c_{cg} - c_{ca}, \\ A_3 &= c_{ca} - G_{c3}, & S_{gs} &= S_{gL} \end{aligned} \quad (32)$$

$$\begin{aligned} A_1 &= (q_{D3}/q_{D2})a_{w3} - c_{wa}, & A_2 &= c_{wa} - c_{wg}, \\ A_3 &= G_{w3} - c_{wa}, & S_{gs} &= S_{gL} \end{aligned} \quad (33)$$

$$\begin{aligned} A_1 &= (q_{D1}/q_{D2})a_{c1} - c_{ca}, & A_2 &= c_{ca} - c_{cg}, \\ A_3 &= G_{c1} - c_{ca}, & S_{gs} &= S_{gT} \end{aligned} \quad (34)$$

$$\begin{aligned} A_1 &= c_{wa} - (q_{D1}/q_{D2})a_{w1}, & A_2 &= c_{wg} - c_{wa}, \\ A_3 &= c_{wa} - G_{w1}, & S_{gs} &= S_{gT}. \end{aligned} \quad (35)$$

[24] Note that it is necessary to estimate q_{D2} and q_{D3} iteratively except for the special case when the injection composition is free of water (i.e., $a_{w1} = 0$) and the initial reservoir composition is free of CO₂ (i.e., $a_{c3} = 0$).

4. Pure Injection and Reservoir Fluids

[25] Hereafter, it is assumed that the injection fluid is free of water and the reservoir fluid is initially free of CO₂. As a result,

$$G_{c1} = 1 - S_s, \quad a_{c1} = 1, \quad G_{w1} = 0, \quad a_{w1} = 0, \quad (36)$$

$$G_{c3} = 0, \quad a_{c3} = 0, \quad G_{w3} = \omega_{wb}\rho_b/\rho_c, \quad a_{w3} = \omega_{wb}\rho_b/\rho_c \quad (37)$$

where ρ_b [ML⁻³] and ω_{wb} [-] are the density and water mass fraction, respectively, for brine free of CO₂. Note that $\omega_{wb} + \omega_{sb} = 1$, where ω_{sb} [-] is the salt mass fraction for brine free of CO₂.

[26] Since $a_{w1} = G_{w1} = 0$, S_{gT} can be calculated from equation (35) without knowledge of q_{D2} and q_{D2} can then be calculated from equation (28). Similarly, since $a_{c3} = G_{c3} = 0$, S_{gL} can be calculated from equation (32) without knowledge of q_{D3} , and q_{D3} can then be calculated from equation (27).

[27] The volumetric saturation of precipitated salt, S_s , can be calculated as follows. The mass of brine evaporated is equal to $2\pi\phi H\rho_b(1 - S_{gT})r_T$, where r_T [L] is the radial distance to the trailing shock. The mass of salt precipitated is equal to $2\pi\phi H\omega_{sb}\rho_b(1 - S_{gT})r_T$. The volume of the salt is equal to $2\pi\phi H\omega_{sb}(\rho_b/\rho_s)(1 - S_{gT})r_T$, where ρ_s [ML⁻³] is the density of precipitated salt. The volume of porespace contained within the trailing shock is equal to $2\pi\phi Hr_T$. Therefore, the volumetric saturation of precipitated salt is found from [Zeidouni et al., 2009]

$$S_s = \frac{\omega_{sb}\rho_b(1 - S_{gT})}{\rho_s}. \quad (38)$$

[28] As discussed earlier, when $z_T < z_C$, it is known that $S_{gT} = 1 - S_{ar}$. For most realistic values of S_{ar} it can be assumed $z_T < z_C$.

5. Application of Darcy's Law

[29] Invoking Darcy's Law:

$$q_a = -\frac{kk_{ra}}{\mu_a} \frac{dP}{dr} \quad (39)$$

$$q_g = -\frac{kk_{rg}}{\mu_g} \frac{dP}{dr} \quad (40)$$

where k [L²] is permeability, P [ML⁻¹ T⁻²] is fluid pressure, and k_{ra} [-], μ_a [ML⁻¹ T⁻¹], k_{rg} [-], and μ_g [ML⁻¹ T⁻¹] are the relative permeabilities and dynamic viscosities of the aqueous and gas phase, respectively, the fractional flow equation for f_g can be written as,

$$f_g = \left(1 + \frac{\mu_g k_{ra}}{\mu_a k_{rg}}\right)^{-1}. \quad (41)$$

[30] Without much loss of generality, the relative permeability functions can be assumed to take the form of power-laws:

$$k_{ra} = k_{ra0} \left(\frac{1 - S_g - S_{ar}}{1 - S_{gc} - S_{ar}} \right)^m, \quad (42)$$

$$k_{rg} = k_{rg0} \left(\frac{S_g - S_{gc}}{1 - S_{gc} - S_{ar}} \right)^n, \quad (43)$$

where S_{ar} [-] is residual aqueous phase saturation and S_{gc} [-] is critical gas saturation, and k_{ra0} [-], k_{rg0} [-], m [-], and n [-] are end-point relative permeabilities and power law exponents for the aqueous and gas phases, respectively.

[31] The substitution of equations (43) and (42) into equation (41) leads to

$$f_g = \left[1 + \gamma \left(\frac{1 - S_g - S_{ar}}{1 - S_{gc} - S_{ar}} \right)^m \left(\frac{S_g - S_{gc}}{1 - S_{gc} - S_{ar}} \right)^{-n} \right]^{-1}, \quad (44)$$

where

$$\gamma = \frac{\mu_g k_{ra0}}{\mu_a k_{rg0}} \quad (45)$$

and differentiating equation (44) with respect to S_g leads to

$$\frac{df_g}{dS_g} = f_g(1-f_g) \left[\frac{n(1-S_g-S_{ar}) + m(S_g-S_{gc})}{(S_g-S_{gc})(1-S_g-S_{ar})} \right]. \quad (46)$$

[32] Interestingly, Figure 1 shows plots of df_g/dS_g (which is linearly proportional to z) against S_g for different values of m and n . For nonlinear relative permeability, S_g is multivalued for given values of df_g/dS_g [Buckley and Leverett, 1942]. For the special case when relative permeabilities are linear functions of S_g , S_g is single-valued for given values of df_g/dS_g and there is an inner region, $df_g/dS_g < 0.4$, where $S_g = 1 - S_{ar}$. Furthermore, it can be seen that this special case gradually develops as m and $n \rightarrow 1$ (note the two inflection points present for the case when $m = n = 1.1$). See Appendix A for further clarification in this respect.

6. Linear Relative Permeability Functions

[33] It is not possible to obtain closed-form solutions for S_{gT} and S_{gL} by substituting equation (46) into equation (31). However, for the special case when $m = n = 1$ (i.e., when k_{rg} and k_{ra} are linear functions of S_g), equations (44) and (46) reduce to

$$f_g = \left[1 + \gamma \left(\frac{1-S_g-S_{ar}}{S_g-S_{gc}} \right) \right]^{-1} \quad (47)$$

and

$$\frac{df_g}{dS_g} = \frac{\gamma(1-S_{gc}-S_{ar})f_g^2}{(S_g-S_{gc})^2}, \quad (48)$$

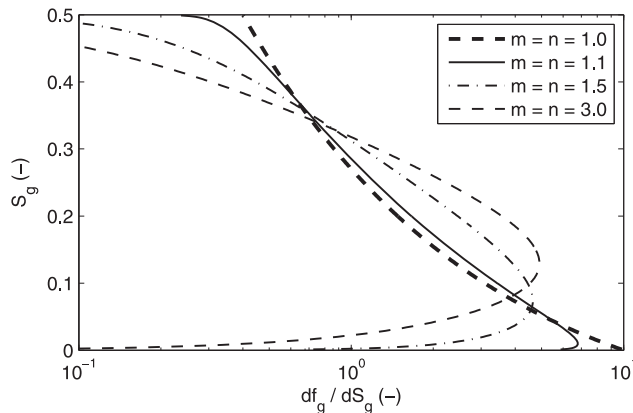


Figure 1. Plots of S_g against df_g/dS_g for different powers according to equation (46) with $\gamma = 0.2$, $S_{gc} = 0$, and $S_{ar} = 0.5$.

which on substitution into equation (31) and solving for S_{gs} leads to

$$S_{gs} = A_4 + \left\{ \frac{\gamma(1-S_{gc}-S_{ar})(A_4A_2+A_3)}{(1-\gamma)[(1-\gamma)A_1+A_2]} \right\}^{\frac{1}{2}}, \quad (49)$$

where

$$A_4 = \frac{S_{gc}(A_1+A_2) - \gamma(1-S_{ar})A_1}{(1-\gamma)A_1+A_2} \quad (50)$$

allowing the gas saturations at the leading and trailing shocks to be obtained directly using equations (32) and (35), respectively.

[34] Recalling equation (29) and invoking equations (36) and (37), equation (48) can also be rearranged to get

$$S_g = \begin{cases} 1 - S_s, & 0 \leq z < z_T \\ 1 - S_{ar}, & z_T \leq z \leq z_C \\ S_{gc} + \frac{(1-S_{gc}-S_{ar})}{(1-\gamma)} \left[\left(\frac{z_C}{z} \right)^{\frac{1}{2}} - \gamma \right], & z_C < z \leq z_L \\ 0, & z > z_L, \end{cases} \quad (51)$$

where

$$z_C = \frac{q_{D2}\gamma}{(1-S_{gc}-S_{ar})}. \quad (52)$$

[35] Note that when $z < z_C$, $S_g = 1 - S_{ar}$. Moreover, when $z_T < z_C$, z_T is no longer located at the beginning of the spreading wave. Consequently, for this special case, equation (31) is invalid for z_T . However, knowing that when $z_T < z_C$, $S_{gT} = 1 - S_{ar}$, and $f_{gT} = 1$, it follows from equation (22) that

$$z_T = \frac{q_{D2}c_{wg}}{c_{wa}S_{ar} + c_{wg}(1-S_{ar})}, \quad z_T < z_C, \quad (53)$$

where q_{D2} is obtained from equation (28).

7. Solving for Pressure

[36] To obtain an equation for pressure, we return to Darcy's law,

$$q_a + q_g = -k \left(\frac{k_{ra}}{\mu_a} + \frac{k_{rg}}{\mu_g} \right) \frac{dP}{dr}. \quad (54)$$

Applying the similarity transform, z , and the q_D identity (equations (3) and (11)), and then rearranging leads to

$$\frac{dP}{dz} = -\frac{M_0}{4\pi\rho_c Hk} \left(\frac{k_{ra}}{\mu_a} + \frac{k_{rg}}{\mu_g} \right)^{-1} \frac{q_D}{z}. \quad (55)$$

Then given our knowledge of the shock fronts, z_T and z_L ,

$$\frac{dP}{dz} = -\frac{M_0}{4\pi\rho_c Hk} \begin{cases} \frac{\mu_c q_{D1}}{k_{rs} z}, & 0 \leq z < z_T \\ \left(\frac{k_{ra}}{\mu_a} + \frac{k_{rg}}{\mu_g} \right)^{-1} \frac{q_{D2}}{z}, & z_T \leq z \leq z_L \\ \frac{\mu_b q_{D3}}{z}, & z > z_L, \end{cases} \quad (56)$$

where k_{rs} [–] is the permeability reduction factor due to salt precipitation and μ_c [$\text{ML}^{-1} \text{T}^{-1}$] and μ_b [$\text{ML}^{-1} \text{T}^{-1}$] are the dynamic viscosities of water-free CO_2 and CO_2 -free brine, respectively.

[37] Integrating with respect to z then yields,

$$P - P_0 = \begin{cases} \frac{M_0}{4\pi\rho_c Hk} \left\{ \frac{\mu_c q_{D1}}{k_{rs}} \ln\left(\frac{z_T}{z}\right) + \mu_g q_{D2} F_2(z_T) + \mu_b q_{D3} F_1(z_L) \right\}, & 0 \leq z < z_T \\ \mu_g q_{D2} F_2(z) + \mu_b q_{D3} F_1(z_L), & z_T \leq z \leq z_L \\ \mu_b q_{D3} F_1(z), & z > z_L, \end{cases} \quad (57)$$

where P_0 [$\text{ML}^{-1} \text{T}^{-2}$] is the initial pressure, $F_1(z) = -\ln z + F_0$ and F_0 is an integration constant yet to be defined, and

$$F_2(z) = -\frac{1}{\mu_g} \int_z^{z_L} \left(\frac{k_{ra}}{\mu_a} + \frac{k_{rg}}{\mu_g} \right)^{-1} \frac{1}{z} dz. \quad (58)$$

[38] Following through the matched asymptotic expansions approach of Mathias *et al.* [2009c, 2011], it can be shown that for a circular closed aquifer of radial extent, r_E [L], (compare with equations (25) and (42) of Mathias *et al.* [2011])

$$F_1(z) = \begin{cases} E_1(\alpha z), & z_E > \frac{0.5615}{\alpha} \\ (\alpha z_E)^{-1} - \frac{3}{2} + \ln\left(\frac{z_E}{z}\right) + \frac{z - z_L}{z_E}, & z_E < \frac{0.5615}{\alpha} \end{cases} \quad (59)$$

where

$$\alpha = \frac{M_0 \mu_b (c_r + c_b)}{4\pi H \rho_c k}, \quad z_E = \frac{\pi \phi \rho_c H r_E^2}{M_0 t}, \quad (60)$$

and E_1 denotes the En function with $n = 1$ (related to the exponential integral function, $\text{Ei}[x]$, via $E_1[x] = -\text{Ei}[-x]$) and c_r [$\text{M}^{-1} \text{LT}^2$] and c_b [$\text{M}^{-1} \text{LT}^2$] are the compressibilities of rock and brine (free of CO_2), respectively.

[39] For an open aquifer of infinite lateral extent, $z_E \rightarrow \infty$ and

$$F_1(z) = E_1(\alpha z). \quad (61)$$

Invoking linear relative permeability function, by virtue of equation (51), equation (58) can be evaluated to obtain

$$F_2(z) = \frac{2}{k_{rg0}} \begin{cases} \frac{1}{2} \ln\left(\frac{z_C}{z}\right) + \frac{z_L^{1/2} - z_C^{1/2}}{z_C^{1/2}}, & z \leq z_C \\ \frac{z_L^{1/2} - z^{1/2}}{z_C^{1/2}}, & z > z_C. \end{cases} \quad (62)$$

8. Comparison With TOUGH2 ECO2N

[40] Results from the analytical solution were compared against those from the two-dimensional TOUGH2 simulations previously presented by Mathias *et al.* [2011]. The models assume a fully penetrating well situated at the origin of a two-dimensional radially symmetric flow field of radial extent, r_E . It is also assumed that the relationship between effective brine saturation, S_e [–], and capillary pressure, P_c [$\text{ML}^{-1} \text{T}^{-2}$], is [van Genuchten, 1980]

$$S_e = \left(1 + \left| \frac{P_c}{P_{c0}} \right|^{n_v} \right)^{-m_v}, \quad n_v = \frac{1}{1 - m_v}, \quad (63)$$

and that brine and CO_2 relative permeability are a linear function of S_e . In the absence of residual CO_2 saturation and salt precipitation, effective brine saturation is defined by $S_e = (S_a - S_{ar}) / (1 - S_{ar})$. The values of the model parameters used are given in Table 1. Further details are provided by Mathias *et al.* [2011]. The effect of salt precipitation on permeability was ignored.

[41] The analytical solution was evaluated using CO_2 and brine properties from equations of state provided by Hassanzadeh *et al.* [2008]. These incorporate work from a number of authors including Batzle and Wang [1992], Fenghour *et al.* [1998], Spycher *et al.* [2003], and Spycher and Pruess [2005]. Following Mathias *et al.* [2011], fluid properties were estimated using a preliminary estimate of well pressure (with fluid properties calculated using the initial pressure) that occurs when the pressure disturbance meets the outer boundary of the reservoir (i.e., $z_E = 0.5615/\alpha$). Consequently, a different set of fluid properties was applied to each of the four scenarios studied. These are detailed in Table 2.

Table 1. Parameters Used for the TOUGH2 Simulations

Parameter
Injection rate, $M_0 = 100 \text{ kg s}^{-1}$
Well radius, $r_w = 0.2 \text{ m}$
Radial extent, $r_E = 20 \text{ km}$
Porosity, $\phi = 0.2$
Rock compressibility, $c_r = 4.5 \times 10^{-10} \text{ Pa}^{-1}$
Initial pressure, $P_0 = 10 \text{ MPa}$
Temperature, $T = 40^\circ \text{C}$
Mass fraction of salt in brine, $\omega_{sb} = 0.15$
Residual brine saturation, $S_{ar} = 0.5$
Critical gas saturation, $S_{gc} = 0$
End-point relative permeability for CO_2 , $k_{rg0} = 0.3$
End-point relative permeability for brine, $k_{ra0} = 1.0$
Permeability reduction factor because of salt precipitation, $k_{rs} = 1$
van Genuchten parameter, $m_v = 0.46$
van Genuchten parameter, $P_{c0} = 19,600 \text{ Pa}$
Formation thickness, $H = 50 \text{ or } 200 \text{ m}$
Permeability, $k = 10^{-13} \text{ or } 10^{-12} \text{ m}^2$

Table 2. Values of Fluid Properties, q_{D2} and q_{D3} for the Four Scenarios Studied

	a	b	c	d
H (m)	50	50	200	200
k (m ²)	10^{-13}	10^{-12}	10^{-13}	10^{-12}
P_{ref} (MPa)	25.13	12.01	14.53	10.58
$\rho_c = \rho_g$ (kg m ⁻³)	869	692	746	647
ρ_b (kg m ⁻³)	1100	1100	1100	1100
ρ_a (kg m ⁻³)	1104	1104	1104	1104
ρ_s (kg m ⁻³)	2160	2160	2160	2160
$\mu_c = \mu_g$ (cP)	0.0847	0.0558	0.0630	0.0507
$\mu_b = \mu_a$ (cP)	0.963	0.963	0.963	0.963
c_b (Pa ⁻¹)	3.54×10^{-10}	3.54×10^{-10}	3.54×10^{-10}	3.54×10^{-10}
ω_{ca} (—)	0.0318	0.0282	0.0289	0.0277
ω_{wg} (—)	0.0021	0.0018	0.0019	0.0016
q_{D2} (—)	1.0003	1.0006	1.0005	1.0006
q_{D3} (—)	0.9821	0.9479	0.9606	0.9355

[42] Figures 1a–1d show the time series of well pressures. The markers are from TOUGH2 simulations and the lines from the analytical solution. The circles and solid lines are output from models that account for partial miscibility of CO₂ and brine. The dashed lines are output from the analytical solution previously presented by *Mathias et al.* [2011], which assumes fully immiscible displacement. Recall that it is the extension of *Mathias et al.* [2011] to account for partially miscible flow, which is the main focus of the current article. Note that well pressures plotted from the two-dimensional radially symmetric TOUGH2 simulation have been vertically averaged.

[43] As discussed in *Mathias et al.* [2011], the distinctive feature between the partially miscible and immiscible simulations is the reduction in pressure rate increase that occurs after 1 hr (1.14×10^{-4} yr). The new analytical solution for partially miscible flow is able to accurately predict this decline in pressure and closely follows the model output from the TOUGH2 simulations.

[44] The cause of the decline is due to the development of the dry-out zone leading to consumption of residual brine and a corresponding increase in CO₂ relative permeability around the well. This can be further understood by studying the saturation and pressure profile plots given in Figure 3. Again, the results plotted from the TOUGH2 simulation have been vertically averaged. The analytical solution is seen to accurately simulate both the extent of the dry-out zone and the saturation of precipitated salt. Similarly, the analytical solution accurately predicts the change in the pressure gradient that occurs in the dry-out zone. Pressures from the immiscible analytical solution of *Mathias et al.* [2011] are shown for comparison.

[45] The effect of CO₂ dissolution into brine manifests itself in two respects. First, in the presence of the leading shock fronts of the saturation profiles (see Figure 3a). Second, in a slight reduction in pressure that occurs at early times (see Figure 2d). The latter effect results from the corresponding reduction in volumetric flow rate, as shown by the q_{D3} values in Table 2. Note that q_{D2} is virtually one, indicating that brine evaporation has little effect on volumetric flow rate.

[46] From a first glance of Figure 2, there is a temptation to dismiss the difference between the partially miscible and miscible simulations, as both simulations converge with

large time following the pressure disturbance meeting the outer boundary of the reservoir, which has been arbitrarily set at 20 km from the injection well. However, should the outer boundary be situated further away, equation (59) dictates that pressure will continue to increase along the same linear-log slope, and the miscible and immiscible simulations will continue to diverge. Nevertheless, considering Figure 2c and applying a pressure constraint of 15 MPa, the immiscible model predicts that one can inject for just 8 yr, whereas the miscible model allows injection to continue for up to 22 yr, almost three times as long.

[47] The derivation of the above analytical solution has involved a number of simplifying assumptions including: vertical pressure equilibrium, negligible capillary pressure, and constant fluid properties. However, these three assumptions have been relaxed for the TOUGH2 simulations. As previously discussed by *Mathias et al.* [2011], the constant fluid properties assumption is reasonable providing an estimate of final pressure is used to calculate CO₂ fluid properties. From the comparison of the well pressures in Figure 2, it is clear that both the vertical pressure equilibrium and negligible capillary pressure assumptions are also reasonable for estimating vertically averaged well pressures.

[48] Figure 4 shows profile plots for the case of $k = 10^{-13}$ m² and $H = 200$ m. The vertical pressure equilibrium assumption is less realistic for this case, as compared to that presented in Figure 3, due to the larger formation thickness. Rigorous inclusion of gravity in the vertically averaged formulation gives rise to an additional second-order (diffusive like) term in the saturation equation [*Nordbotten and Celia*, 2006; *MacMinn and Juanes*, 2009; *Juanes et al.*, 2010]. Accordingly, there is a notable discrepancy between the vertically averaged gas saturation at 10 yr estimated by the analytical solution and the TOUGH2 simulation. Specifically, gravity segregation has caused the extent of the CO₂ plume to travel further in the TOUGH2 simulation. Nevertheless, as seen in Figures 3 and 4, the analytical solution is able to accurately approximate the radial extent of the dry-out zone, the level of salt precipitation, and the vertically averaged pressure distribution. The reason is that the dry-out zone and the pressures are controlled by the larger velocities situated close around the injection well, which are mostly horizontal due to the horizontal driving force provided by the injection well boundary.

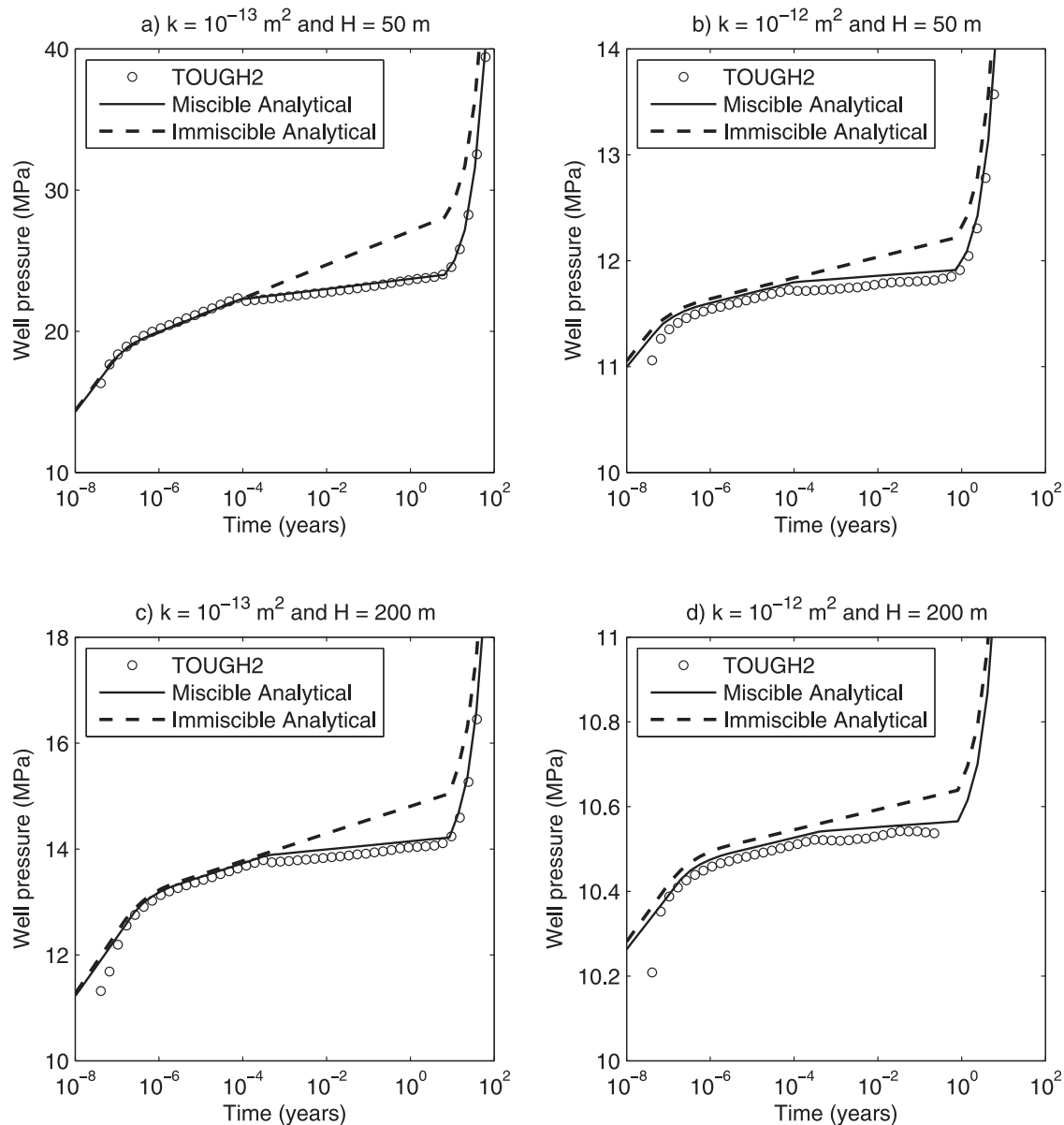


Figure 2. Comparison of well pressures for the four different scenarios (Figures 1a–1d). Results from TOUGH2 have been vertically averaged.

[49] With regard to capillary pressure, according to the simulations studied, there is no significant effect on vertically averaged well pressure (again compare to the results shown in Figure 2). Recall from Mathias *et al.* [2011], the capillary pressure parameters used are the same as previously adopted by Zhou *et al.* [2008]. Of interest is that the dry-out zone can potentially lead to strong capillary forces where CO₂ will tend to reimbibe toward the well, increasing the amount of salt precipitated in the dry-out zone. Accounting for counter-current imbibition is found to be particularly important when seeking to estimate the quantity of CO₂ that becomes residually trapped after injection has ceased [Javaheri and Jessen, 2011]. But comparing results from models which ignored and included capillary pressure (and in turn, counter-current imbibition), Pruess and Muller [2009] found that inclusion of capillary pressure effects is unlikely to increase salt precipitation by more than

a factor of order 1.1. Furthermore, notable changes in the shape of the dry-out zone, as a result of counter-current imbibition, were only observed for the exceptionally small injection rate of 0.25 kg s⁻¹ (see Figure 7 in the work of Pruess and Muller [2009]). Injection rates of practical interest for commercial scale projects typically range from 3 to 120 kg s⁻¹ [Oldenburg *et al.*, 2004; Zhou *et al.*, 2008]. In the current study, an injection rate of 100 kg s⁻¹ is assumed.

9. Summary and Conclusions

[50] The objective of this study was to extend the pressure buildup equations of Mathias *et al.* [2009c, 2011] to account for effects associated with the partial miscibility of CO₂ and brine. These include evaporation of water into the CO₂ rich phase, dissolution of CO₂ into brine, and salt precipitation. This was achieved by applying two-component

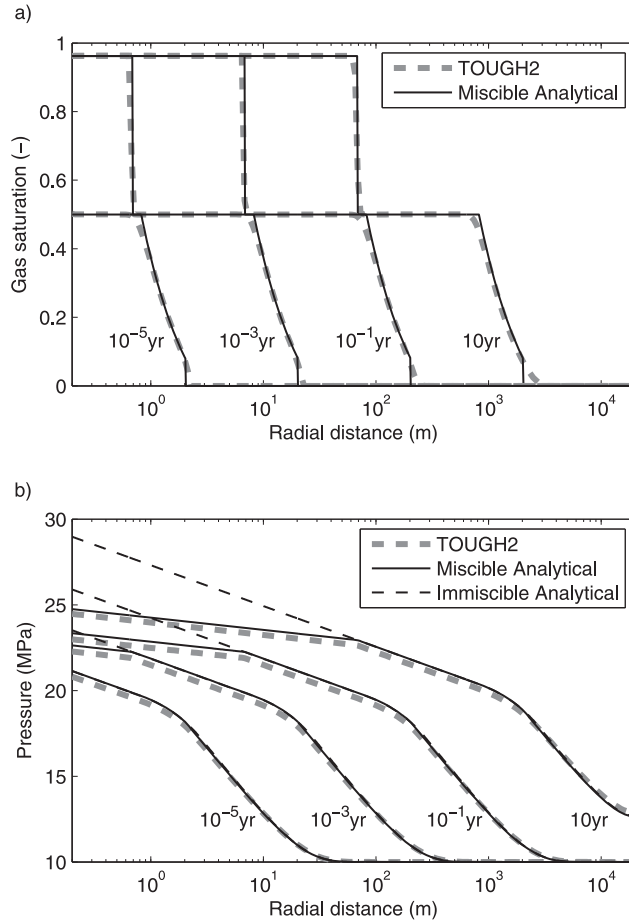


Figure 3. Comparison of (a) gas saturation and (b) pressure distributions for the scenario shown in Figure 2a, i.e., $k = 10^{-13} \text{ m}^2$ and $H = 50 \text{ m}$. Results from TOUGH2 have been vertically averaged.

two-phase fractional flow theory [Orr, 2007] in conjunction with linear relative permeability functions, to derive a gas saturation distribution function (equation (51)). From this, the relative permeability distribution was obtained and integrated to obtain the new pressure buildup equation, equation (57). In general (i.e., for arbitrary relative permeability functions), the evaluation of equation (57) requires the numerical integration of equation (58). But for the special situation when relative permeability is a linear function of saturation, equation (58) integrates exactly to yield the closed-form expression given in equation (62).

[51] Similar equations have previously been presented by Burton *et al.* [2008]. However, the difference here is that we additionally account for volume change on mixing and provide closed-form expressions for the location of the shock fronts for the special case when relative permeability is a linear function of saturation (obtained using either equations (30), (48), and (49) or equation (53)). Furthermore, the pressure equations can be used to describe both closed and open aquifers (using either equations (59) or (61)).

[52] The analytical solution was tested by comparison against output from TOUGH2 ECO2N, previously presented by Mathias *et al.* [2009c]. Results from the analytical solution were obtained using fluid properties provided by equations of state documented by Hassanzadeh *et al.* [2008]. The

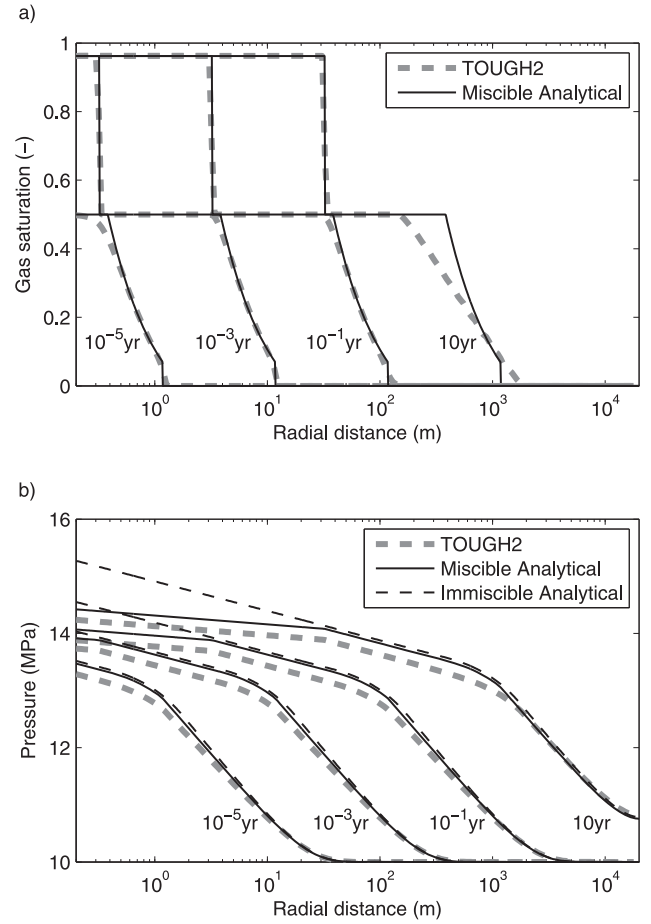


Figure 4. Comparison of (a) gas saturation and (b) pressure distributions for the scenario shown in Figure 2c, i.e., $k = 10^{-13} \text{ m}^2$ and $H = 200 \text{ m}$. Results from TOUGH2 have been vertically averaged.

analytical solution was compared to results from TOUGH2 and found to accurately approximate the extent of the dry-out zone around the well, the resulting permeability enhancement due to residual brine evaporation, the volumetric saturation of precipitated salt, and the vertically averaged pressure distribution in both space and time for the four scenarios studied.

[53] While the effect of brine evaporation can be considerable, the effect of CO_2 dissolution is small. CO_2 dissolution into brine leads to a modest reduction in volumetric flow rate beyond the two-phase region, resulting in a reduction in pressure that occurs throughout injection. For the scenarios studied, volumetric flow rate reduction was found to be less than 7% and the effect on pressure was barely noticeable.

[54] The resulting equations remain simple to evaluate in spreadsheet software, and can be easily implemented in currently available storage capacity estimation frameworks [e.g., Mathias *et al.*, 2009a].

Appendix A: Shock Construction With Linear Relative Permeability

[55] Figure 1 illustrates an unusual feature of the linear relative permeability function, namely that the inflection points in the S_g versus df_g/dS_g function are lost. Linear

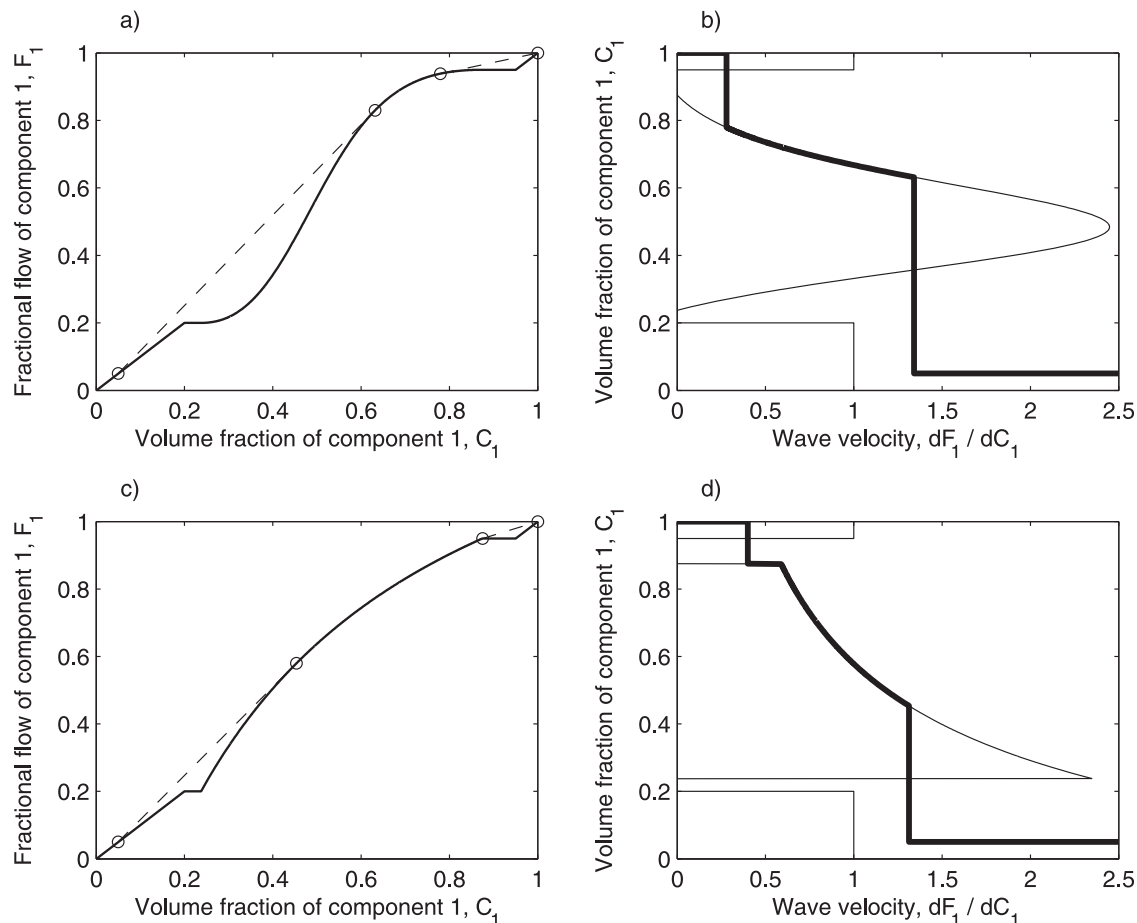


Figure 5. Plots explaining the leading and trailing shock constructions for the example presented by Orr [2007, be sure this isn't linked to Figure 4 of this article]. Figures 5a and 5b show results assuming quadratic relative permeability. Figures 5c and 5d show results assuming linear relative permeability. The location of the shocks are found from the gradients of the dashed lines in 5a and 5c. (b, d) Complete fractional flow functions and final solutions with shocks in place are plotted as thinner and thicker lines, respectively.

relative permeability therefore leads to situations where the trailing shock is not located at the beginning of the spreading wave (recall equation (53)). This point is demonstrated further in Figure 5, which compares the example previously presented by Orr [2007, his Figure 4.9], assuming quadratic relative permeability (i.e., with equations (42) and (43) and $m = n = 2$), with an identical example assuming linear relative permeability (i.e., $m = n = 1$).

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